

# RAW MATERIALS

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## STRUCTURAL-PHASE TRANSFORMATIONS IN FIRING OF A NEW CERAMIC MATERIAL: TOPAZ-BEARING ROCK

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The specifics of the chemicominalogical composition of the topaz-bearing raw material from the Kopna deposit and the phase-formation process in thermal treatment of topaz-bearing rocks with different ratios between the topaz and quartz components are considered. The expedience of using this material in the technology of refractory and engineering aluminosilicate ceramics is established. Owing to the good reinforcing properties, the needle-shaped and filament mullite formed in decomposition of topaz can be used in various composite materials based on glass, ceramics, polymers, etc.

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The current shortage of domestic high-quality aluminosilicate materials, including refractory clays for ceramic production, the need for using elevated temperatures for the synthesis of mullite from other alumina materials of natural (alumina hydrates and silicates) or artificial (technical alumina, electrocorundum) origin, and the high cost of the latter motivate the testing of such nontraditional aluminosilicate minerals as topaz in the production of mullite.

The considerable promise of topaz as a possible material for various ceramic technologies stems from its very nature, since topaz is a fluoraluminosilicate  $\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$  with the following content (%): 48 – 62 alumina, 28 – 39 silica, 12 – 20 fluorine. The heating of pure topaz (starting at a temperature of 850 – 900°C) is accompanied by a substantial weight loss due to the removal of fluorine in the form of silicon fluoride  $\text{SiF}_4$  with the density decreasing from 3.36 to 3.08 g/cm<sup>3</sup>, and after firing at 1500°C topaz represents virtually pure mullite of a clearly expressed needle habitus.

The first data on the use of topaz for aluminosilicate refractories appeared in the literature in the 1940s, when a deposit of topaz material was discovered in the USA and the Brever mine was developed [1]. As the deposit was exhausted, publication of new data regarding this material notably declined.

The revival of interest in topaz in Russia is related to the discovery of topaz rocks at the Kopna deposit (Kemerovo Region) located in convenient geographic and economical conditions: the deposit is accessible for mining and is near the industrial centers of Kuzbass. A specific feature of the

ore from this deposit is its complex gold-quartz-topaz composition with a variable ratio of topaz to quartz.

Preliminary prospecting of the topaz and quartz-topaz rocks of the Kopna deposit indicate the advisability of using them in production of refractory materials, clear and opacified glass, self-glazing porcelain materials, alumina from depleted nepheline ore, etc. [2 – 4]. Of all possible areas of application of topaz, the ceramic technologies are the most interesting.

It is known that the most significant service parameters of ceramic materials can be controlled by influencing the properties of a structure in synthesis. We have previously established the mineralizing effect of small quantities (up to 0.5 – 1.0%) of proper topaz on the phase-formation process in kaolinite clays, which is manifested in a more active formation of mullite and cristobalite, a simultaneous decrease in the temperature of their synthesis, and the improvement of the structure of mullite of the traditional (prismatic) habitus [5].

The purpose of the present paper was to investigate the possibility of using topaz material from the Kopna deposit in the technology of aluminosilicate ceramics. Six samples of topaz-bearing rocks with different ratios of topaz to quartz were investigated. The results of the chemical analysis of the samples are listed in Table 1.

Since the theoretical quantity of  $\text{SiO}_2$  bonded in the topaz structure is 32.96%, an increased content of silica in the total chemical composition points to the presence of free quartz-bearing material. Furthermore, a specific feature of

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the chemical composition of the considered rocks is that they are nearly free of other impurities.

The qualitative and quantitative estimates of the mineralogical composition of the rocks using x-ray phase analysis and the calculations (taking into account the chemical composition) indicate the presence of only two minerals registered by the x-ray phase analysis, i.e., quartz and topaz; furthermore, the first five samples (T1 – T5) can be classified as quartz-topaz, and sample T6 is a finely dispersed (below 0.088 mm) topaz concentrate, which is a product of flotation concentration of a topaz-bearing rock (Table 2).

The IR absorption spectrum of the raw (unfired) topaz concentrate with a maximum content of the rock-forming mineral T6 exhibits intense bands in the low-frequency spectrum range of 600 – 700  $\text{cm}^{-1}$ , a multiplet band in the range of 800 – 1000  $\text{cm}^{-1}$ , some less intense bands in the range of 300 – 500 and 1170  $\text{cm}^{-1}$ , a weak band at 780  $\text{cm}^{-1}$ , and very intense absorption bands in the high-frequency range of 2800 – 3700  $\text{cm}^{-1}$  (Fig. 1)

Since topaz belongs to the insular fluoroaluminosilicates, its crystalline structure is typically represented by a combination of tetrahedral  $[\text{SiO}_4]$  and octahedral  $[\text{Al}(\text{F}, \text{OH})_2\text{O}_4]$  groups. The tetrahedrons do not have other common vertexes, and the octahedrons are connected with each other by their vertexes; each of the four vertexes is linked to one tetrahedron. The octahedrons are further linked by common edges made up of two oxygen ions into chains positioned parallel to the  $c$  axis. Oxygen, fluorine, and hydroxyl ions regularly alternate parallel to axis (010) in the densest hexagonal packing of spheres. The electrostatic valence rule is strictly observed, since the oxygen ion is linked to one silicon ion and two aluminum ions from the groups  $[\text{SiO}_4]$  and  $[\text{Al}(\text{F}, \text{OH})_2\text{O}_4]$ , and each hydroxyl or fluorine ion is linked to two aluminum ions [6].

Therefore, the appearance of three intense absorption bands with minimums at 1170, 870, and 830  $\text{cm}^{-1}$ , a less intense band at 1050  $\text{cm}^{-1}$ , and a weak diffuse band at 1000  $\text{cm}^{-1}$ , as well as 470, 450, and 390  $\text{cm}^{-1}$  in the IR spectrum of the topaz concentrate, is caused by the valence and deformation vibrations of Si – O in the insular radical of  $\text{SiO}_4$ . The absorption bands with minimums at 680, 620, 560, and 540  $\text{cm}^{-1}$  belong to the valence vibrations of Si – O – Al(VI) – O.

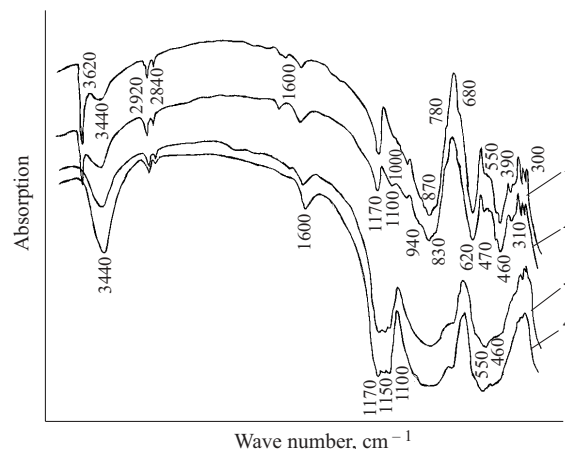


Fig. 1. IR absorption spectra of topaz concentrate (1) and the products of its heat treatment at 850 (2), 1100 (3), and 1350°C (4).

Furthermore, two absorption bands with minimums at 3660 and 3440  $\text{cm}^{-1}$  are present in the high-frequency range of the considered spectrum, which may be due to different reasons: either the existence of two types of hydrogen bonds with different energy in the topaz structure, since these bands characterize two different distances of Al – OH and, consequently, two types of  $\text{Al}(\text{O}, \text{OH})_6$  octahedrons, or partial isomorphic substitution of the  $\text{F}^{-1}$  ion for the  $\text{OH}^{-1}$  groups localized in the octahedral positions, or both reasons simultaneously.

It is known that the end product of topaz decomposition is mullite; therefore, it is interesting to study in detail the physicochemical processes occurring under the thermal destruction of proper topaz and of topaz naturally mixed with other mineral components of the topaz-containing rock. For this purpose, we analyzed the topaz concentrate with the highest topaz content among the rocks considered (T6), as well as the topaz rocks, in which the impurity (quartz) content prevails over the topaz content (T3 – T5). The thermal treatment was carried out at temperatures ranging from 850 to 1350°C with at least 1 h exposure at the maximum temperature.

The diffraction patterns of all heat-treated products obtained on a DRON-3M diffractometer under  $\text{CuK}_\alpha$  radiation qualitatively differ in the presence of x-ray maximums typi-

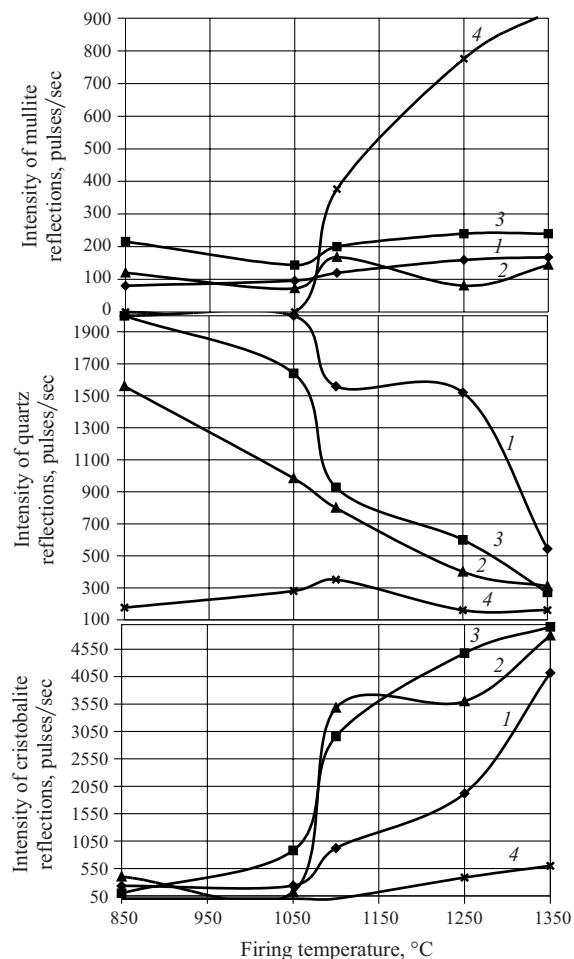
TABLE 1

Sample	Weight content, %					
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	calcination loss*
T1	92.80	3.43	1.20	0.71	0.51	1.35
T2	85.14	8.29	0.56	0.67	0.95	4.59
T3	82.94	10.20	0.79	0.70	0.10	5.27
T4	79.97	11.20	0.79	0.60	1.40	6.04
T5	75.94	15.70	0.37	0.20	0.70	7.49
T6	59.65	26.25	0.35	0.10	1.31	12.34

\* Calcination at a temperature of 1350°C.

TABLE 2

Rock	Content of, %		
	quartz	topaz	other minerals
T1	90.8	7.3	1.9
T2	80.3	17.7	2.0
T3	77.0	21.8	1.2
T4	73.4	23.9	2.7
T5	65.7	33.0	1.3
T6	43.0	56.0	2.0



**Fig. 2.** Intensities of x-ray reflections of mullite ( $d = 0.540$  nm), quartz ( $d = 0.423$  nm), and cristobalite ( $d = 0.404$  nm) versus the firing temperature of topaz rocks: 1, 2, 3, and 4) rocks T3, T4, T5, and T6, respectively.

cal of only mullite, cristobalite, and quartz and, occasionally, of non-transformed topaz. An analysis of the obtained dependences of the diffraction reflection intensities of the main crystalline phases on the firing temperature indicated that the formation of mullite and the inversion of quartz proceed differently in rocks with different ratios of topaz to the impurity component (Fig. 2).

It is established that for the topaz concentrate (T6) with a prevalence of topaz over quartz, firing up to a temperature of  $1350^{\circ}\text{C}$  does not ensure a complete transformation of topaz, which is evidenced by the presence of the reflections of residual topaz in the diffraction patterns of the heat-treatment products. Moreover, mullite can be identified by the x-ray analysis only starting at  $1100^{\circ}\text{C}$ , and the reflections of the emerging mullite have a high resolution and significant intensity, which indicates the perfection of its crystalline structure and its substantial quantitative content. An increase in the firing temperature up to  $1350^{\circ}\text{C}$  intensifies the mullite formation process (Fig. 2, curve 4).

An analysis of the diffraction patterns of the products of decomposition of the quartz-topaz rocks, in which quartz clearly prevails over topaz (T3 – T5), established a significant effect of the mineralogical composition of topaz rocks on the phase-formation process in firing.

Mullite is identified in all topaz rocks containing quartz from 77% (T3) to 65.7% (T5) already at a temperature of  $850^{\circ}\text{C}$ , but its reflections have low intensity and are blurred, which points to an imperfect structure, and as the temperature further increases, the intensity of the reflections does not significantly change (Fig. 2, curves 1 – 3).

The appearance of the cristobalite reflections in the diffraction patterns of T3 – T5 rocks simultaneously with the mullite emerging at a temperature of  $850^{\circ}\text{C}$  shows that cristobalite, along with mullite, is the second product of the decomposition of topaz. The sharp increase in the intensity of the respective x-ray reflections of cristobalite (Fig. 2, curves 1 – 3) at a firing temperature over  $1100^{\circ}\text{C}$  is determined by the transformation of the impurity quartz in these rocks.

Thus, the effect of the quartz component on the mullite formation is registered under the thermal dissociation of topaz, which acts as the initiator of the process in the case of its prevalence in the phase composition of the rock. The reason for this activating effect, in our opinion, should be looked for in the microheterogeneous structure of the considered topaz rock, since it is known that quartz and topaz in the ore from this particular deposit have complex structural interrelationships, mostly in the form of isomorphic fine-crystalline aggregates with a prevailing grain size of  $0.03 - 0.05$  mm and with typical fine accretions and mutual intergrowth of these minerals [7].

According to the contemporary concept of the synthesis of solids, an initial process in the formation of a new phase is the formation of microseeds either on the surface or in the whole volume of the initial phase. Therefore, when microsites of topaz are contained in the bulk of a quartz rock (when quartz prevails over topaz), the restructuring of the lattice can occur both in the volume of a topaz grain and on the surface of the topaz-quartz interface. As the packing of the oxygen ions in the emerging mullite is similar to such packing in quartz, mullite seeds may originate on the quartz surface and the oxygen sublattice at the quartz-mullite interface boundary remains almost continuous. Such a similarity of the emerging phase (mullite) and the substrate phase (quartz) facilitates the seed formation; consequently, a modification of the topaz structure starts at a lower temperature. A significant role in this process is played by the gaseous components of the topaz decomposition, since the gas phase is a medium for transferring material from one particle to another.

The structural transformations occurring in dissociation of topaz are manifested in the IR absorption spectra of the products of heat treatment of the topaz concentrate (T6). It is confirmed that decomposition of topaz in the rocks with a prevailing topaz content is registered only starting at a tem-

perature of 1100°C, since heating up to 850°C produces virtually no differences between the IR spectra of the initial rock and the heat-treated rock (Fig. 1, curves 1 and 2), and only when the treatment temperature grows to 1100°C or more does the spectroscopic pattern of the products of thermal destruction of topaz change. In particular, a whole set of absorption bands disappear or become modified due to the rupture or deformation of Si–O bonds in the silicon-oxygen tetrahedron of topaz and impurity quartz (the absorption bands at 1050, 1000, 470, and 390  $\text{cm}^{-1}$  disappear, a doublet in the range of 830–870  $\text{cm}^{-1}$  transforms into a wide band with minimums at 870 and 390  $\text{cm}^{-1}$ ). The rupture of the bonds between the tetrahedral and the octahedral groups in the insular topaz structure is manifested in the disappearance of the absorption bands with minimums at 680, 620, 560, and 540  $\text{cm}^{-1}$  related to the valence vibrations of Si–O–Al(IV)–O. The disappearance of an intense absorption band in the high-frequency spectrum range with a minimum at 3620  $\text{cm}^{-1}$  is caused by the dehydration and defluorination of topaz. The conservation of the absorption bands at 2840, 2920, and 3440  $\text{cm}^{-1}$  in the same spectrum range indicates an incomplete destruction of topaz up to 1350°C, which is also substantiated by the x-ray phase analysis data.

A qualitative indication of the mullite formation within the temperature range of 1000–1350°C is the transformation of the intense absorption band with a minimum at 1170  $\text{cm}^{-1}$  into a wide multiplet band with minimums at 1170, 1150, and 1100  $\text{cm}^{-1}$ .

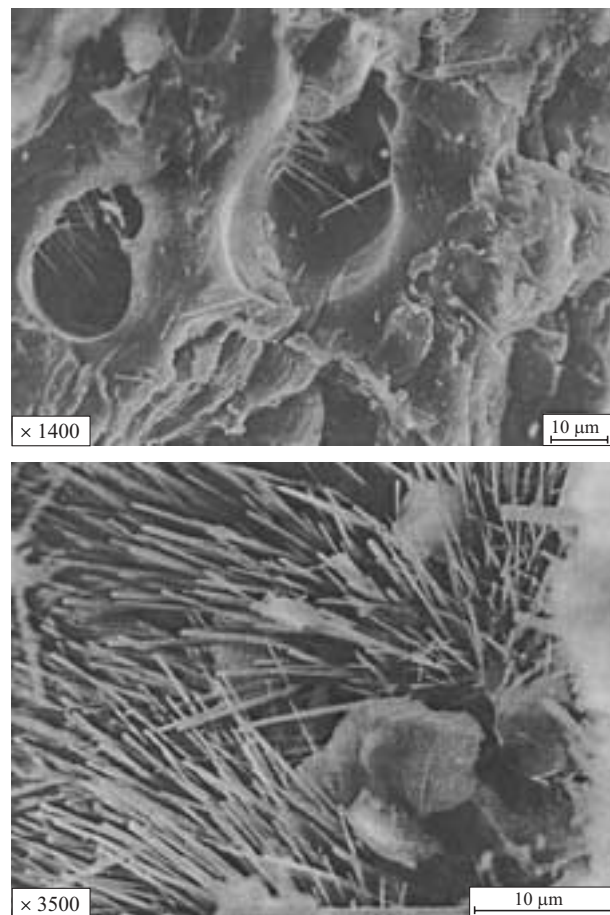
For visual evaluation of the size and shape of the emerging mullite crystals, electron microscopy was used.

A microphoto (Fig. 3) shows rounded pores with fused edges of size 10–30  $\mu\text{m}$ . Under subsolidus temperatures, as the material passes into a thermoplastic state, the pores become spheroidized due to a viscous flow and acquire the shape of craters. The pores are filled with mullite crystals shaped as needles 10  $\mu\text{m}$  long or smaller. Needle-shaped mullite crystals over 40–50  $\mu\text{m}$  long are observed on the sample surface as well. In both cases, the filament shape of the crystals freely grown on the grain surface and inside the pores is a convincing symptom of their vapor-phase origin.

Studies of the chemicomineralogical composition of natural topaz-containing material and the phase formation processes under thermal dissociation of topaz in the rock demonstrated the advisability of using this material in the technologies of aluminosilicate refractories and engineering ceramics. Due to its good reinforcing properties, the needle-shaped and filament mullite formed in decomposition of topaz can be used in various composite materials based on glass, ceramics, polymers, rubber, etc.

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**Fig. 3.** Microstructure of the products of firing of topaz concentrate at 1350°C.

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